1.0	4.5	2.8	2.5
	5.0	3.2	2.2
		3.6	
1.1		4.0	2.0
			1.8
1.25	1.4		1.6

MICROCOPY RESOLUTION TEST CHART

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Studies of Metal-Silicon, Silicon-Metal, and Silicide Based Interfaces:
Synchrotron Radiation Photoemission and Inverse Photoemission Investigations
of Interface Formation and Compound Nucleation

FINAL REPORT

John H. Weaver, PI

15 January 1988

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University of Minnesota
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Minneapolis, Minnesota 55455

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This report summarizes a three-year investigation of metal/semiconductor interface formation. Highlights for the 21 refereed papers are included, together with copies of feature articles published in *Physics Today* and *The American Scientist* which cite support from ARO.

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2. S.A. Chambers, T.R. Greenlee, G.A. Howell, and J.H. Weaver, "Quantitative Interdiffusion Studies of Noble Metal/Si(111)-7x7 Interfaces by Angle-Resolved Auger Electron Emission," J. Vac. Sci. Technol. A **3**, 1291-1294 (1985).

3. S.A. Chambers and J.H. Weaver, "Thermally Induced Structural and Compositional Modification of the Cu/Si(111)-7x7 Interface," J. Vac. Sci. Technol. A **3**, 1929-1934 (1985).

4. J.H. Weaver, "Metal/Semiconductor Interfaces," *Physics Today* **39**, 24-30 (January 1986). Feature article and cover photo of instrument purchased, in part, through this grant.

5. M. del Giudice, M. Grioni, J.J. Joyce, M.W. Ruckman, S.A. Chambers, and J.H. Weaver, "Modeling Homogeneous and Heterogeneous Metal/Semiconductor Interface Reactions with Photoemission and Angle Resolved Auger Spectroscopies," Surf. Sci. **168**, 309-322 (1986).

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20. J.H. Weaver, "Synchrotron Radiation Photoemission Studies of Interfaces," Chapter 2 in *Analysis and Characterization of Thin Films*, edited by K.N. Tu and R. Rosenberg, Treatise on Materials Science and Technology, Vol. 27 (Academic Press) (in press).

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--M. Grioni, Postdoctoral Fellow
--S.A. Chambers, Postdoctoral Fellow
--M. del Giudice, Postdoctoral Fellow
--D.M. Hill, PhD Student
--C.M. Aldao, PhD Student
--J.J. Joyce, PhD Student - Degree awarded May 1987

Summary of Research Findings

The focus of all our studies has been the interfacial region formed when metal and semiconductor overlayers are grown by atomic vapor deposition on semiconductor surfaces. We have sought to elucidate the physics and chemistry of the evolving interfaces, examining epitaxial systems, amorphous systems, and systems which exhibit substantial amounts of intermixing and compound formation. To accomplish these goals, we have used high resolution synchrotron radiation photoemission, x-ray photoemission, low energy electron diffraction, angle resolved Auger diffraction, and inverse photoemission.

Our studies have resulted in the publication of 22 refereed papers, including feature articles in *Physics Today* and *American Scientist*. The cover of *Physics Today* in January 1986 showed the small spot x-ray photoelectron spectrometer that was purchased with ARO support during the summer of 1985. We have reported the results at a wide variety of national and international meetings, giving both invited and contributed papers.

Early emphasis was on the detailed characterization of evolving Si-based interfaces. We have examined the noble metals (Cu and Au), Ce, Ti, V, and Ca because these systems afforded a broad perspective from which to model interactions. In studies of the interactions of the noble metals with Si, we have shown that thin, ordered overlayers of Cu can be formed on Si(111) through photoemission and Auger spectroscopies. We then triggered extensive intermixing of Cu/Si and characterized the in-diffusion of Cu and the out-diffusion of Si. Comparison of these results to analogous information obtained for Au/Si, which does not form an ordered overlayer but reacts immediately, demonstrated the much greater in-diffusion of Au relative to Cu. Finally, we examined the effects of thermal treatments on these Cu/Si intermixed interfaces and showed that Cu can be made to desorb and that the Si which is left behind grows epitaxially on the substrate but retains a monolayer skin of silicide. As a corollary experiment, we used high resolution energy loss spectroscopy with H as a marker to compare reactivity and bond character of the clean and Cu-terminated Si(111) surfaces.

Our research with reactive metal overlayers on silicon has shown that reacted interfacial zones are both simpler and more complicated than has generally been thought. We have shown that well-defined species form, even at room temperature. By following the evolving interface as a function of overlayer thickness, we have shown that each species forms in a way which is limited by kinetics and bulk thermodynamics. This last point is particularly important because it indicates that thermodynamic concepts can be applied to very thin interfaces -- that partitioning of the reaction products can be described by the lever rule, that each phase is stable and is not consumed, and that the interface is laterally and vertically heterogeneous. Despite this heterogeneity, our modeling has been very successful. These results were extremely important and led to a much better microscopic understanding of interface properties.

Another series of interface investigations also examined the morphologies and reactivities of metal/semiconductor interfaces using photoelectron spectroscopy as the primary technique. One of the most significant results came from the Cr/Ge system, where we approached the problem from a number of different perspectives. Initially, we studied the reactivities and phase formation for Cr when it interacts with crystalline Ge(111) and compared that behavior with Cr interacting with amorphous Ge. The goal was to determine whether the reaction products would be the same despite disorder and the associated additional channels for diffusion and reaction. We found, indeed, that there were major differences, with the amorphous substrate displaying a range of chemical environments not found for the crystalline substrate. Likewise, we found differences related to the thickness of the Ge substrate which involved the mass balance of reactants. Subsequently, we investigated interface formation for the inverted interface formed by depositing Ge onto Cr film substrates. This study revealed the Ge/Cr interface to be atomically abrupt, in stark contrast to the intermixed Cr/Ge interface. This observation was quite a surprise and we continued with

comparisons of metal/semiconductor and semiconductor/metal interfaces to understand the basic mechanisms which drive intermixing in such dimensionally-constructed systems.

As one of the follow-on studies of inverted interfaces, we investigated the formation of the Ge/Au interface. This was significant because it was known that Au induces substantial disruption when deposited onto Ge. We were able to characterize this system in detail, showing that the interfaces are markedly non-symmetric in their properties. In particular, the Au/Ge system exhibits a spatially heterogeneous interface in which the Ge content varies with distance from the buried interface to the free surface. We examined the distribution in detail, found that surface segregation can be modeled and characterized, and that segregation produces a surface layer which has substantial amounts of Ge. Beneath this skin, there is a Au layer with small amounts of Ge in solution. In contrast, the Ge/Au system exhibits a threshold for reaction and a very limited range over which the Au-Ge mixture forms. These studies were very important for understanding atom profiles at interfaces. These results ultimately led to the writing of a chapter on segregation at semiconductors surfaces (citation #22).

Another thrust emphasized the formation of the Co/Si interface, and we used high resolution synchrotron radiation photoemission and angle resolved Auger spectroscopy. We were able to show that the first reaction product for the room temperature interface is very thin and serves to act as a diffusion barrier against subsequent intermixing. This study led to an extended examination of diffusion at interfaces in which we sought to determine diffusion coefficients and activation energies. Structural studies of the annealed interface showed that there is the formation of epitaxial $CoSi_2$ which is rotated 180° relative to the surface normal. Moreover, epitaxial clusters of more than a single thickness formed at low coverages, indicating a heterogeneous surface. Finally, we found evidence for Si termination of the outermost silicide layer. This latter observation was particularly important for studies of Si epitaxial growth on $CoSi_2$ and for investigations of the reactivity of silicide overlayers. Subsequent studies of the structure of M/Si studies emphasized Ce overlayers. Detailed investigations revealed ordering in several different configurations - ordering which would not have been predicted based on the tendency of Ce to react with Si to form silicides.

Some of the most exciting developments of the second and third years involved temperature dependent studies of dynamic processes which occur at metal/semiconductor interfaces. In particular, we sought to describe the evolution of an interface at elevated temperatures where kinetic constraints are different from those at 300 K. These studies built on the extensive work that we and others had done at room temperature while breaking new ground by emphasizing kinetics.

Several major studies were completed for the V/Ge system. We measured the photoemission core level lineshape as a function of V coverage and the temperature of the system and were able to determine the spatial scale over which the reaction products was formed. At room temperature, the germanide thickness was determined to ~14 Å. If the amount of V exceeded 14 Å, then a solid solution of Ge in V was observed to form, limited by diffusion. The effect of changing temperature was to enhance the range over which the germanide formed and to induce the formation of a germanium-rich grain boundary phase. These studies were conducted at temperatures between 300 and 653 K. With the photoemission results, we determined through detailed mathematical modeling the controlling parameters for interface evolution, namely the activation energy and the amounts of each phase which formed.

The second major series of dynamic experiments emphasized the buried interface for Ti and Cr overlayers grown on GaAs(100). By using the high resolution XPS system with tunable surface sensitivity, we were able to determine the distribution of the atomic species in these interfaces. At room temperature, we found that the deposition of 15 Å of metal induced relatively limited amounts of substrate disruption (3.5 and 5 Å, respectively). Increasing the temperature enhanced the reaction, but again we were able to quantitatively describe the retreat of the buried interface. Sputter profiling provided detailed information about the outdiffusion of Ga and the stability of the interface. These studies of the buried interface were unique and were very important.

Another major experiment involved the use of CoSi$_2$ as a diffusion barrier to block atomic intermixing at Au/Si interfaces. Detailed synchrotron radiation photoemission experiments showed that the effectiveness of the barrier depended critically on the amount of Co that was deposited. In particular, we found that when the deposited amount was less than 3.5 Å of Co, the extent of intermixing was only slightly altered. However, when the coverage exceeded 3.5 Å, the extent of intermixing was sharply reduced. Analysis showed that 3.5 Å deposition corresponds to the completion of an epitaxial CoSi$_2$ layer on Si of thickness ~13 Å. These results suggested that CoSi$_2$ would be an excellent diffusion barrier. At the same time, its epitaxial nature offers the opportunity to grow ordered overlayers on it. Subsequently, we undertook temperature dependent experiments to investigate the stability of the CoSi$_2$ layer and its ability to withstand indiffusion of Au diffusion into Si.

Finally, late in the funding cycle, we performed a series of experiments that examined the dynamic behavior of the Ge/Si heterojunction. Atomic diffusion and the kinetics of epitaxial Ge/Si alloy formation at the Ge/Si(111)-(7x7) heterojunction in the temperature range 20-700°C were measured *in situ* using high resolution Al K$_\alpha$ x-ray photoemission spectroscopy, scanning electron microscopy, and low energy electron diffraction. With XPS it was possible to determine the rate of Si redistribution in the overlayer. Ge films were grown by thermal evaporation onto sputter-annealed Si substrates at 20 and 300°C in an ultra-high vacuum environment. The relative photoemission intensities from the Ge 3d and Si 2p core levels, measured as a function of overlayer thickness, revealed the spatial distribution of Si and Ge and the abruptness of the boundary. Ar$^+$ ion sputter profiles confirmed the atomic distribution. At higher temperatures, LEED patterns showed the transition from disordered to ordered overlayer growth, and the XPS results showed strong intermixing. The XPS results were being modeled with Fick's laws to obtain diffusion coefficients and effective activation energies for the predominant diffusion mechanisms.

The results of these many experiments suggested that a most promising avenue for subsequent studies would involve dynamic process. ARO sponsorship of this work was reported via a proposal submitted in February 1987. That proposal is still pending.

Characterization of intermixing at metal-semiconductor interfaces by angle-resolved Auger-electron emission: Cu/Si(111)-7×7

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$Si(L_{2,3}VV)$ and $Cu(M_{2,3}VV)$ Auger intensities from the Cu/Si(111)-7×7 interface have been measured in a polar-angle-resolved fashion for various Cu thicknesses. A simple theory of polar-angle-resolved Auger emission has been developed and used to extract atom-number densities for both Si and Cu as a function of depth. It is found that significant Si outdiffusion is triggered at 300 K by Cu coverage in excess of 2 Å with characteristic diffusion lengths for Si of ~35% of the overlayer thickness. Cu diffusion into the substrate, if it occurs at all, is limited to characteristic penetration depths of 1 to 2 Å for all coverages. The increased extent of Si outdiffusion above 2 Å is accompanied by substantial changes in Cu distribution throughout the interfacial region; at 2 Å, the Cu density increases sharply from interface boundary to surface whereas above 2 Å, the Cu density is constant throughout the interface.

I. INTRODUCTION

Condensation of metal atoms on single-crystal semiconductor surfaces leads to a wide variety of interesting physical and chemical phenomena.[1] Ordered layer-by-layer growth, cluster formation,[2] interdiffusion,[3,4] and chemical reaction[5] have been observed for different systems. Successful observation of these phenomena requires a wide repertoire of experimental probes; no one technique can provide all the necessary information to unambiguously model the microscopic development of the interface.

In this paper we address the issue of interdiffusion at a metal-semiconductor interface. This research was undertaken because knowledge of the atomic densities of the substrate and adsorbed material as a function of depth in the interface region is critical for characterizing interface properties. Most attempts to obtain such information have utilized argon-ion sputter profiling.[6-11] As discussed by some of these authors,[6-8] ion-induced surface damage, preferential sputter rates, implantation of sputtered species, depth calibration problems, and poor depth resolution render the quantitative reliability of this technique dubious, particularly when applied to ultrathin overlayers (a few angstroms). In order to overcome these difficulties, attempts have been made to obtain a better understanding of the sputtering process[9,11] and to quantitatively account for the phenomenon of sputter broadening.[9]

A nondestructive alternative to sputter profiling which eliminates many of the above problems utilizes the polar-angle dependence of Auger and photoelectrons emitted from both the substrate and overlayer. As originally demonstrated by Fadley and Bergstrom,[12] varying the collection angle relative to the plane of the surface leads to selective enhancement of bulk and surface signals. Most such studies to date have utilized core-level photoelectrons excited by either conventional x-ray sources[13] or synchrotron radiation.[14] One disadvantage of polar-angle resolved photoemission is that of data acquisition time. In order to obtain a complete polar intensity profile, a large number of spectra must be taken over the collection angle range 0° to 90°. A minimum of nine or ten spectra would allow a rough polar profile to be constructed, but 20 to 40 spectra would be desirable. Active metal overlayers will contaminate in the several-hour time span required to acquire such detailed data by means of photoemission.

A closely related yet much faster approach to the problem involves utilizing the polar-angle dependence of low-energy core-valence-valence (CVV) Auger-electron intensity. An excellent spectrum can be obtained in the pulse-counting $N(E)$ mode in just a few minutes. Moreover, low incident beam currents (a fraction of a microampere) can be used to minimize surface damage, and one still obtains very high count rates. In this article we describe the first use of polar-angle-resolved Auger emission to quantitatively study interdiffusion phenomena at a metal-semiconductor interface. The Cu/Si(111)-7×7 system was chosen because interdiffusion of Si into the overlayer has been observed and qualitatively studied with other surface analysis techniques,[3,4] including x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), Auger-electron spectroscopy (AES), and low-energy electron diffraction (LEED).

This article is organized as follows: Section II describes the theory of polar-angle-resolved Auger emission as

Quantitative interdiffusion studies of noble metal/Si(111)-7×7 interfaces by angle-resolved Auger electron emission

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Polar-angle resolved Auger electron emission and related modeling have been used to determine quantitative details of composition and diffusion phenomena in the Cu/Si(111) and Au/Si(111) interface systems. The extent of Si outdiffusion increases with coverage in a gradual fashion for Au, with characteristic diffusion lengths (CDL) ranging from 18% of the overlayer thickness at a 2 Å coverage to 39% at 20 Å. In contrast, Si CDL values in Cu increase abruptly from 20% of the overlayer thickness at 2 Å to ~35% at coverages from 5 to 20 Å. Au diffuses deeply into the Si substrate, whereas Cu indiffuses only slightly (CDL = 1–2 Å). These model predictions are consistent with the more substantial lattice disruption brought about by Au, leading to no long-range order in the overlayer, and the persistent diffusion of Si to the surface of 150-Å-thick Au overlayers.

Evaporation of metal overlayers on single-crystal semiconductor surfaces at room temperature often results in substantial interdiffusion, a phenomenon not frequently observed in metal–metal or gas–metal chemisorption systems. Quantitative characterization of such interfaces places a new challenge before experimentalists. Although ion sputter depth profiling may be useful for semiquantitative characterization of thick overlayers, its utility in studying thin overlayers ($\lesssim 20$ Å) is limited. It seems that a nondestructive method of depth profiling that is sensitive to ultrathin metal overlayers would be of considerable value. In this article we describe the first application of polar-angle resolved Auger electron emission to the quantitative characterization of metal–Si interfaces. We have chosen the noble metals Cu and Au because both are qualitatively known to intermix with Si.[1–4]

We make use of the fact that varying the polar angle θ relative to the surface leads to selective enhancement of surface or bulk signals.[5] At a given polar angle θ, the Auger intensity from a component characterized by an atom number density function $\rho(y)$ within the overlayer is given by[6]

$$I(\theta) = \left(\frac{I_0 \sigma A \Omega D}{\sin^2 \alpha}\right)(1-R)\left(\frac{\sin \theta'}{\sin \theta}\right)\int_0^\infty \rho(y)$$
$$\times \exp(-y/\Lambda \sin \theta')dy. \quad (1)$$

I_0 and A are the incident electron beam flux and cross-sectional area, respectively; σ is the Auger cross section; Ω is the solid angle of acceptance; D is the detector efficiency; α is the angle of incidence with respect to the surface; R is the electron reflection coefficient for Auger electrons passing through the surface potential barrier; θ' and θ are the propagation angles inside and outside the material, respectively; and Λ is the electron mean free path. The perpendicular depth y is measured relative to the surface. In order to utilize Eq. (1) to determine $\rho(y)$ for components in an interface, the group of factors outside the integral [collectively referred to hereafter as $F(\theta)$] must be evaluated separately for pure substrate and overlayer materials. This task is readily accomplished by measuring $I(\theta)$ for atomically smooth surfaces of pure metal and semiconductor, and solving Eq. (1) for $F(\theta)$, recognizing that $\rho(y)$ is simply the bulk density of the material. Equation (1) can then be evaluated for both metal and semiconductor in a particular interface using $F(\theta)$ and physically reasonable choices for $\rho(y)$. Theory can then be fit to experiment to determine the optimal choice for $\rho(y)$.

We have employed an Auger electron spectrometer with angle-resolving capability described elsewhere.[7] Single-crystal wafers of Si(111) were cleaned in situ by cycles of Ar ion bombardment and annealing to 800 °C. The resulting surfaces showed a sharp reconstructed 7×7 LEED pattern and were free of contaminants, as judged by Auger spectra collected at $\theta = 10°$ relative to the surface.

High-purity Cu and Au were separately evaporated onto a Si substrate using a quartz-crystal oscillator to monitor coverage. Pressures never exceeded 2×10^{-10} Torr at any stage of evaporation or measurement (base pressure = 4×10^{-11} Torr). Polar scans were constructed from spectra taken every 2° from $\theta = 90°$ (normal emission) to $\theta = 0°$. LEED shows that at coverages above ~10 Å, the Cu/Si(111) surface is ordered with a (111) orientation rotated 30° with respect to the substrate. Therefore, polar scans in two symmetry inequivalent azimuthal planes perpendicular to the surface were taken and averaged to remove intensity fluctuations due to diffraction effects. Since Au overlayers are disordered, polar scans in only a single azimuthal plane were collected.

In Figs. 1 and 2, we show Auger spectra as a function of coverage for the Cu and Au interfaces. In the bottom spectrum in each figure, sufficient metal has been deposited to bury essentially all the Si, even though at 150 Å a small amount of Si diffuses to the surface of the Au overlayer. Polar profiles taken at these coverages are used to determine $F(\theta)$ for pure Cu and Au, although a slight correction is necessary for the latter to account for the small amount of Si still

Thermally induced structural and compositional modification of the Cu/Si(111)-7×7 interface

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We have investigated the morphology, local composition, and surface stoichiometry of the annealed Cu/Si(111)-7×7 interface using scanning electron microscopy, scanning Auger microscopy, characteristic x-ray emission spectroscopy, and angle-resolved Auger emission. It is found that annealing of intermixed Cu/Si phases with copper thickness between 5 and 20 Å at temperatures of ~600 °C causes most of the Cu to evaporate. The Si which had been in the intermixed phase recrystallizes in the form of submicron-sized islands. The Cu which does not evaporate forms a very stable Cu₃Si-like skin which uniformly covers the surface. This morphology is very different from what has been reported for Ag/Si (Ag island formation) or Au/Si (micron-sized Au islands with silicide skin) and can be related to the kinetics of Cu desorption and the initial intermixed phase.

I. INTRODUCTION

There has been a great deal of very good research which has described the microscopic properties of representative metal/silicon interfaces at room temperature.[1-4] Remarkably enough however, the influence of temperature on the reactions which occur has not been extensively examined. Initial studies with noble-metal/silicon systems suggested that annealing simply promotes segregation of the metal overlayer into islands which are large on an atomic scale.[5,6] In contrast, Calliari *et al.*[7] have shown that Au island formation does occur upon annealing but that the islands are covered with a thin skin of intermixed Au–Si character. Their work clearly demonstrated that the dynamics of thermally induced atomic rearrangement are more complicated than previously thought.

The purpose of the present paper is to describe the temperature dependent behavior of a model system, Cu/Si, since it is known to form a reacted or intermixed interface at ~300[8] and 100 K.[9] We present scanning electron microscopy (SEM), scanning Auger microprobe (SAM), and angle resolved Auger electron spectroscopy (ARAES) results which indicate that the intermixed Cu/Si(111) interface undergoes very unusual morphological and composition changes for a wide range of coverages and temperatures. Indeed, we will show that the annealed Cu/Si system exhibits qualitatively different behavior than either Au/Si or Ag/Si because Si recrystallizes and forms islands on the annealed surface—not metal islands as previously thought. We will relate that behavior to the kinetics of Cu desorption from the intermixed phase.

Two interesting studies have recently dealt with the temperature dependent morphology of the Ag/Si(111) and Cu/Si(111) interfaces. SEM work by Venables *et al.*[5] with Ag/Si(111) has shown that annealing at temperatures ranging from ~420 to 500 °C caused the Ag overlayers to segregate into micron-sized, three-dimensional islands, even for coverages as low as 8 monolayers (ML). Those results demonstrated a Stranski–Krastanov (SK) growth mode (ordered metal overlayer plus metallic islands). Subsequent work on the annealed Cu/Si(111) interface by Ringeisen *et al.*[6] yielded LEED, AES, XPS, and UPS evidence which is consistent with SK growth at coverages in the range of 1 to 40 ML, plus an SEM image at 75 ML which looked very much like what was obtained for Ag/Si(111) over a wider range of coverages. By analogy, then, it was concluded that Cu would exhibit SK growth at all coverages. This conclusion was particularly intriguing because of the very different behavior of Cu/Si and Ag/Si at room temperature (intermixed vs abrupt interfaces). The present study therefore extends the very nice work of Ringeisen *et al.*[6] to higher temperature and verifies their experimental results but, through the use of additional experimental probes, comes to quite different conclusions concerning the nature of the interface.

II. EXPERIMENTAL

ARAES and LEED measurements were performed in a system described in detail elsewhere.[8,10] The sample consisted of a (111) oriented *p*-type Si wafer which was cleaned *in situ* by Ar ion sputtering and annealing to 900 °C. The resulting surface showed the characteristic 7×7 LEED pattern and was atomically clean. Cu evaporation was carried out at pressures $<2\times10^{-10}$ Torr and was monitored with a quartz crystal oscillator. The sample was at room temperature. Annealing at temperatures ranging from ~400 to 650 °C was performed by electron bombardment from the back. Temperatures were measured with an infrared optical pyrometer. Typical operating pressures were $7-9\times10^{-11}$ Torr. At no time did the surface show any trace of adsorbed C or O, as judged by grazing emission Auger spectra.

SEM and SAM measurements were performed on JEOL JEM 100CX SEM and PHI 595 SAM systems available through the NSF Regional Instrumentation Facility for Surface Analysis of the University of Minnesota. Annealed Cu/Si(111) interfaces were prepared and characterized in the ARAES–LEED chamber and transferred through air to the SEM and SAM chambers.

Metal-semiconductor interfaces

John H. Weaver

Metal-semiconductor interfaces

The mixing of atoms at boundaries produces regions with distinctive properties; the resulting combinations have a wide variety of uses—from smaller microelectronic devices to new, exotic composite materials.

John H. Weaver

In my view of the evolution of solid-state physics, the 1970s were the decade of bulk phenomena. We made enormous strides in understanding crystals—we mapped their energy bands, developed clever computational schemes and became experimentally and theoretically adept at characterizing solid crystals. At the same time, we developed the tools to study surfaces, and we continue to make amazing progress in this area, as Shuk Y. Tong explained in a recent article (PHYSICS TODAY, August 1984, page 50).

Today, the drive to develop ever-smaller microelectronic devices, exotic multicomponent composites, complex catalysts and biological implants is increasing the need to understand interfaces. It seems to me that the 1980s, and possibly the 1990s as well, will be viewed as the decade when we brought boundary regions under microscopic scrutiny.

If the study of interfaces is indeed the next step in solid-state physics, it is a step made possible by all we have learned about bulk and surface phenomena and by the fancy new tools developed to investigate solids and

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surfaces. The excellent work done with crystalline materials and their surfaces makes it possible, for example, to consider interfaces where the atoms are not uniformly distributed; with such interfaces we may be able to create unique atomic structures stabilized by the surrounding material. Furthermore, supercomputers and elegant computational schemes allow quantitative modeling of increasingly complex systems. In light of the wide range of experimental and theoretical tools at our disposal, it appears that the next few years hold great promise for major breakthroughs in our understanding and control of the properties of interfaces.

The interfacial zone

An interfacial zone is a transition region between two different materials. It might be the boundary formed when a metal is deposited onto gallium arsenide in the modulation-doped field-effect transistor diagrammed in figure 1, or the boundary between $NiSi_2$ and silicon in a buried metallic layer of a three-dimensional integrated circuit.

Interface research focuses on the unique properties of such boundary regions. It seeks to understand how the properties of boundary regions differ from those of the bulk solids on either side and how these regions influence

the behavior of the composite. The interface zone can be atomic in scale for abrupt interfaces, or it can extend for tens or hundreds of angstroms for interfaces where the two materials react chemically. The properties of the interface region are influenced by, for example, dimensional constraints (quantum effects), disorder, defects, the formation of compounds, heterogeneity and kinetics. Boundaries are therefore fascinating regions, rich in both scientific challenge and technological importance.[1,2]

Interface research is inherently interdisciplinary, blending experimental and theoretical work in physics, chemistry, materials science and engineering. Many of the issues are so complex that teams of researchers join forces to address them. Not surprisingly, the scientific and technological relevance of interface research have prompted significant cooperation among academic, government and industrial laboratories.

Solid-state physicists are showing increasing interest in a subclass of interface phenomena, namely those at metal–semiconductor interfaces. One indication of this interest is the growing number of meetings and conferences[3] on the subject. One finds wide-ranging discussions of interface phenomena at conferences sponsored by

MODELING HOMOGENEOUS AND HETEROGENEOUS METAL/SEMICONDUCTOR INTERFACE REACTIONS WITH PHOTOEMISSION AND ANGLE-RESOLVED AUGER SPECTROSCOPY

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Insight into the fundamental physical and chemical properties related to interface formation can be gained from high-resolution synchrotron radiation photoemission and angle-resolved Auger spectroscopies. In photoemission, detailed analysis of valence band and core level EDCs makes it possible to follow the formation of metal/semiconductor interfaces to identify the onset of reaction, characterize the chemical species that form, and determine their relative concentrations as a function of coverage. The coverage dependence of the intensity of the individual components of the complex core level EDCs can be related to the morphology of the interface. Complementary information obtained by using angle-resolved Auger provides depth profiling of the reacted interface and a measure of the extent of metal atom diffusion into the semiconductor. We discuss results for interfaces which exhibit an atomically abrupt junction (Ge/Ta(110) and Ge/Cr), interdiffusion and reaction (Ce/Ge(111) and Cr/GaAs(110)), and metal in-diffusion (Cu/Si(111) and Au/Si(111)).

1. Introduction

Interfacial phenomena can be extraordinarily complex. However, their study is both scientifically fundamental and technologically relevant. The purpose of this paper is to briefly examine representative metal/semiconductor interfaces to show how high-resolution synchrotron radiation photoemission and quantitative angle-resolved Auger emission make it possible to model the coverage-dependent morphology of the junction [1].

In fig. 1 we show an evolving interface to emphasize some of the phenomena that are observed. At the top left, we show an array of atoms representing a clean surface, plus several chemisorbed adatoms and a defect. The adsorption of these metal atoms leads to metal–semiconductor bond formation with bond strengths determined by the atoms involved. Interactions among the adatoms, aggregation, and growth will then be influenced by surface mobili-

High-temperature nucleation and silicide formation at the Co/Si(111)-7×7 interface: A structural investigation

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We have investigated the atomic structure of annealed Co/Si(111) interfaces prepared by the evaporation of one-, two-, and thirty-monolayer equivalent coverages of Co. Experimental and theoretical angular distributions of the Co LMM Auger intensity reveal that for all coverages investigated a $CoSi_2$ phase forms which is rotated 180° about the surface normal relative to the substrate. At low coverages, the $CoSi_2$ phase is in the form of clusters which appear to be two to three $CoSi_2$ layers in thickness and are terminated by a Si(111) bilayer. The Si(111) overlayer, which is in addition to the terminal plane of Si atoms associated with the outermost $CoSi_2$ layer, also appears to be rotated 180° about the surface normal relative to the Si substrate.

I. INTRODUCTION

Silicide-Si(111) interfaces involving the near-noble metals Co and Ni have been shown to be abrupt and epitaxial when grown by either metal deposition onto a heated Si substrate or by annealing the interface grown at room temperature.[1-4] This result is expected in light of the close lattice match between the metal silicides and Si. For Co and Ni, the disilicide forms with a calcium fluoride crystal structure and lattice constants of 5.356 Å and 5.406 Å, respectively. Comparison with the Si lattice constant of 5.428 Å shows the mismatch to be 1.3% for $CoSi_2$ and 0.4% for $NiSi_2$. Thus these systems constitute ideal choices for fundamental studies of epitaxial growth and lateral homogeneity in thin silicide films. Moreover, abruptness and epitaxy at a silicide-Si interface make possible the formation of epitaxial heterostructures of the type $Si/MSi_2/Si$, where $M = Co$ or Ni.[5]

Cross-sectional transmission electron microscopy (TEM) measurements have shown that a deposition of a few hundred angstroms of Co onto room-temperature Si(111), followed by annealing at 800–950°C, results in the formation of an epitaxial $CoSi_2$ phase which is rotated 180° about the surface normal with respect to the substrate (the so-called B-type silicides). This result is corroborated by extended electron-energy-loss fine-structure measurements in which silicide phases grown in the same way yield a Co nearest-neighbor distance which is (within experimental error) that expected for $CoSi_2$.[6] In these experiments emphasis was placed on the structure of the extended interface, which is of the order of 100 Å thick.

In this paper we examine the atomic structure for ultrathin $CoSi_2$/Si(111) interfaces. Such studies are of vital importance because atoms in the interfacial layer constitute the template for further crystal growth. We have exploited the intensity anisotropies associated with Co LMM Auger emission from a one-monolayer-equivalent deposition of Co on room-temperature Si(111)-7×7, which was subsequently annealed at 500°C. Comparison of the associated angular distributions with those for the extended B-type $CoSi_2$ phase, as well as those generated by kinematical scattering calculations, permits us to determine the structure and morphology of the ultrathin interfacial layer. This technique has been shown to be a useful tool for structural determination of metal-semiconductor[7] and metal-metal interfaces.[8-10]

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

All measurements were performed on a spectrometer described in detail elsewhere,[11] with the exception of the following modifications. A second electron gun made by Kimball Physics (KP) capable of beam energies up to 10 keV has been added to complement the 5-keV gun built into the cylindrical mirror analyzer (CMA). The angle of incidence of the KP gun is 20° with respect to the polar axis of rotation, in contrast to the CMA gun for which the angle of incidence is 90°. The higher incident energies afforded by the new gun yield better Auger cross sections for deep core-core-core transitions in which the binding energy of the initially ionized core level is of the order of a few keV or more.[12]

In addition, a Digital Equipment Corporation PDP11/23 microcomputer has been incorporated for data acquisition and analysis, replacing the multichannel analyzer used in earlier studies. Auger intensities were determined by Shirley or S-shaped background subtraction[13] and integration following a single 11-point smooth procedure. To ensure that intensities were not affected by variations in incident-beam current, each integrated area was normalized by dividing by the number of counts in an arbitrary channel on the high-kinetic-energy side of the peak of interest. Comparison with angular distributions obtained without normalization in which the primary beam current was carefully monitored throughout the experiment showed that this procedure did not alter the angular distributions in any significant way.

A p-type Si wafer cut and polished to within 1° of the (111) plane was chemically etched, lightly argon-ion sput-

SURFACE STRUCTURAL DETERMINATION OF METAL–SEMICONDUCTOR INTERFACES BY ANGLE-RESOLVED AUGER ELECTRON EMISSION

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In this paper we discuss the use of high-energy Auger electron diffraction as a short-range, local probe of the structural environment of the emitting atom. We have utilized the intensity anisotropies associated with Cu(LMM) emission from the annealed 1 ML Cu/Si(111) interface at shallow take-off angles to elucidate the structure of the surface. Through the use of a kinematical scattering formalism, we have modeled the surface structure in various ways and compared calculated azimuthal intensity profiles with those from experiment to find the optimal geometry. Comparison of theory with experiment suggests that annealing the 1 ML Cu/Si(111) interface briefly to 600°C causes the surface to reconstruct to a planar geometry, with Cu atoms embedded in the six-fold hollow sites at a depth of 0.1 ± 0.1 Å below the surface plane. The calculated angular distributions are a very sensitive function of near-neighbor structure, permitting an accurate determination of the local structural environment.

1. Introduction

Metal–semiconductor interfaces grown at room temperature and at elevated temperature exhibit diversified and interesting structural rearrangements. Interdiffusion [1–3], clustering [4], and preferential desorption [5] result in unique morphologies and atomic distributions at the interface. Unusual reconstructions often lead to complex LEED (low-energy electron diffraction) patterns. An example of this sort of behavior is the Cu/Si(111)-7 × 7 interface. The depostion of 1 ML of Cu followed by mild annealing causes the 7 × 7 reconstruction to convert to a different reconstruction characterized by a complex and rarely observed LEED pattern [1]. In principle, suitable LEED calculations could suggest long-range structures which would be consistent with the observed LEED pattern. However, details of the *local* structural environment of the Cu atoms may not be so easy to deduce for such a complex surface using this technique.

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Comparative study of the formation of Cr/Ge and Ge/Cr thin-film interfaces

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The interface morphologies of Cr/Ge and Ge/Cr thin film junctions have been studied using synchrotron radiation photoemission. Ge 3d and Cr 3p core level results for Ge deposition onto Cr indicate that Ge chemisorbs without disrupting the substrate. With increasing coverage, an amorphous Ge film forms (a-Ge) and buries the abrupt Ge/Cr interface. Examination of the reverse Cr/Ge thin-film interface prepared under identical conditions shows extensive substrate disruption, metal-semiconductor interdiffusion, and a reacted interfacial region. Comparison of this Cr/Ge thin-film interface to Cr/Ge(111) shows analogous Ge outdiffusion and compound formation, demonstrating that disorder in the a-Ge substrate is not the only cause of the enhanced interdiffusion observed for Cr/Ge compared to Ge/Cr. The dissimilar reactivity of Ge/Cr and Cr/Ge is attributed to differing substrate disruption energetics and clustering at the earliest stages of interface formation.

INTRODUCTION

Interfaces between dissimilar materials play an important role in solid state physics[1] and in such technological settings as the microelectronics industry.[2,3] The body of work which has examined interfaces is now very large, and many excellent reviews summarize studies of metal-semiconductor,[4-7] semiconductor-semiconductor,[8] metal-polymer,[9] and metal-metal interfaces.[10] We now know that most metal-semiconductor interfaces exhibit some degree of atomic intermixing, even at room temperature,[4] and that selective compound formation can be enhanced by thermal treatment,[11] choice of substrate, or choice of technique used to deposit the metal.[3,12,13] Likewise, reaction kinetics and interface morphologies can be altered by the presence of surface contaminants.[14,15]

In this paper we examine the process of interface formation at room temperature for Ge condensation from the vapor phase onto polycrystalline chromium film substrates, for Cr deposition onto atomically smooth Ge(111) surfaces prepared by cleaving, and for Cr deposition onto amorphous Ge films. Synchrotron radiation was used for soft-x-ray photoemission studies of the metal and semiconductor core levels. This technique[16] reveals which chemical species are present in the interfaces, whether their local atomic environments change during interface formation, and the spatial distribution of interfacial chemical components. This work is then complementary to characterization of thin film interfaces undertaken by workers using transmission electron microscopy,[17] Rutherford backscattering (RBS),[18] and Auger electron spectroscopy combined with depth profiling.[19] Motivation for the present study was provided by recent experiments which showed the following.

(i) The Ge/Ta(110) interface is atomically abrupt and does not evolve into an extended interface,[20] while the deposition of refractory metals onto Ge(111) (Ref. 21) and Si(111) (Ref. 22) does induce intermixing.

(ii) RBS studies of Co-Si compound formation on Si(111) and amorphous Si films indicated that the growth kinetics varied for the two types of surface.[23]

In interpreting our work on Ge/Ta(110),[20] we proposed that the large heat of formation of Ta metal [188 kcal/mol (Ref. 24)] implied that relatively large amounts of energy would be needed to disrupt the Ta(110) surface. Since Ge did not induce reaction, the energetics of condensation were insufficient. On the other hand, we observed that the heats of formation of Cr, Ge, and several Cr-Ge compounds were comparable in magnitude and concluded that the Cr-Ge system might provide a test of the use of bulk thermodynamic parameters in predicting interface stability.

The present experiment examines in detail the evolution of the Ge 3d core emission [binding energy ~29 eV (Ref. 25)]. By preparing all films and surface under equivalent ultrahigh-vacuum conditions, we were able to compare directly the Ge/Cr and Cr/Ge interfaces, free of any trace of impurities either at the interface or in the bulk of the thin films. Cr deposition on cleaved Ge(111) provided a basis for comparison with the thin film interfaces.

EXPERIMENTAL TECHNIQUES

Thin film preparation and subsequent photoemission studies were done on the 3m toroidal grating monochromator beamline at Wisconsin's Tantalus storage ring. Detailed core level studies were performed using photon energies of $h\nu = 40$ and 75 eV (Ge 3d) and 85 eV (Cr 3p). The Ge 3d core levels were recorded at these energies in order to vary the photoelectron kinetic energies and, hence, the surface sensitivity of the measurements. We estimate an overall resolution of 220 meV at 40 eV and 300 meV at 75 eV. For the Cr 3p core level studies we estimate the resolution to be ~500 meV. The reproducibility in determining the position of different spectral components was ±0.025 eV. The photoelectron spectrometer and UHV system used in this study have been described elsewhere.[26]

Soft-x-ray photoemission study of Cr-Ge intermixing on crystalline and amorphous Ge surfaces

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We have investigated room-temperature interdiffusion and reaction induced by thin Cr films on Ge(111) and on amorphous Ge films of thicknesses between 20 and 120 Å. Soft-x-ray photoemission results show that Cr and Ge intermix to form several Cr-Ge bonding configurations in the extended interfacial zone. Analysis of Ge $3d$ core-level shifts shows that the first and the terminal Cr-induced species which form on a-Ge have the same binding energies as those which form on Ge(111). In contrast, for Cr/a-Ge, we also observe an intermediate constituent which does not form on Ge(111). We attribute the differences in reaction products to microstructural differences in a-Ge which influence the diffusion of Ge and Cr. Comparison of the results as a function of substrate thickness shows that the reaction products are always the same but that the width of the interfacial zone varies with the availability of the semiconductor atoms.

INTRODUCTION

The factors which determine interface profiles are complex and interrelated, involving the electronic configuration of the constituents, reaction kinetics, diffusion rates, details of morphology, and the presence of contaminants. These factors have been examined for a variety of interfaces with a wide range of techniques, and there is a large amount of literature which discusses metal overlayers on crystalline semiconductors.[1] In contrast, much less is known about the corresponding overlayers on amorphous substrates. Indeed, it is not obvious that interfaces formed on crystalline and amorphous semiconductors should be similar. Tsai et al.[2] reported significant variations in reaction kinetics and resultant overlayer morphologies for Au/Si and Au/a-Si:H. Lien et al.[3] found that silicide formation at the Co/Si interface proceeds faster on Si(100) than on amorphous Si. Perfetti and co-workers[4] observed enhanced metal-semiconductor interdiffusion for Au/a-Ge compared to that in Au/Ge(111). These authors have generally attributed their results to the porous nature of the a-Ge films and microstructure differences in the germanide phase. Although amorphous Ge films have similar local bonding character, tetrahedral coordination, and nearest-neighbor distances to those in crystalline Ge,[5] films contain a high density of defects which can act as paths of enhanced diffusion[6] or serve as bonding or nucleation sites.

In this paper, we discuss the room-temperature formation of Cr-Ge compounds following Cr deposition onto crystalline and amorphous Ge. The purpose of this study was to compare in detail the properties of crystalline and amorphous interfaces with transition-metal overlayers. By varying the thickness of the amorphous Ge substrate, we were able to control the amount of Ge available for reaction, and we could investigate variations of the growth of the reaction products. By performing this experiment in ultrahigh-vacuum conditions, we were able to obtain results which reflect the surface chemistry of atomically clean Cr and Ge surfaces.

EXPERIMENTAL TECHNIQUES

Amorphous Ge films of thickness between 20 and 120 Å were evaporated onto thermally cleaned and crystallized Ta(110) foil substrates from resistively heated W baskets. System pressures were held below 2×10^{-10} Torr during Ge evaporation and quickly recovered to operating pressures in the mid-10^{-11}-Torr range. Photoemission studies of the Ta $4f$ levels showed that the as-deposited films exponentially attenuated the substrate emission, indicating that Ta and Ge did not intermix to form Ta-Ge compounds. Photoemission studies showed that the characteristic Ge valence-band features were washed out, that the Ge $3d$ core emission was broadened [full width at half maximum (FWHM) changes ~0.1 eV], and that the Gd $3d$ binding energy shifted 0.2–0.3 eV to lower binding energy, all consistent with the formation of an amorphous Ge layer.[7,8] Likewise, low-energy electron diffraction studies showed the absence of any overlayer ordering.

Ge(111) surfaces were prepared by *in situ* cleaving of n-type Ge bars (Sb doped with resistivity of 5–10 Ω cm). The bars were notched and etched in a HF−HNO$_3$−acetic acid solution prior to insertion into the vacuum system. Cr films were deposited by sublimation from a W basket (source-to-substrate distance ~30 cm). The Cr deposition rate was ~1 Å/min with typical evaporation pressures of ~1×10^{-10} Torr after outgassing of the Cr source. No trace of contamination was detected in the photoemission results obtained from any of these as-deposited films.

All experiments were performed on the 3-m TGM beam line at the Tantalus storage ring. The experimental setup permitted acquisition of angle-integrated photoemission spectra using predominantly s-polarized synchrotron radiation incident on the sample at an angle of ~45°.[9]

Asymmetries in atomic intermixing at Au/Ge and Ge/Au interfaces

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Synchrotron-radiation photoemission was used to study room-temperature intermixing at interfaces prepared by Au evaporation onto amorphous Ge films (a-Ge) and Ge evaporated onto Au films. Our results show that both interfaces develop intermixed regions but that their formation is highly asymmetric. The Au/a-Ge interface is characterized by gradual development of a Au_3Ge-like mixture, the persistence of the mixture to high coverage, and the failure of the system to form a pure Au layer. In contrast, the inverted Ge/Au interface is characterized by weak surface interaction at low coverage, triggering of reaction at about 2 Å to form the Au_3Ge-like mixture, a very limited coverage range over which the mixture develops (2–8 Å), and the growth of a Ge layer containing Au in solution at higher coverage. We conclude that the evolution of Ge/Au interface evolution is similar to that of the transition-metal/semiconductor junctions where fully-reacted products form at the substrate interface, dilute solutions develop farther from the boundary, and the dimensions are controlled by kinetics. This Ge/Au behavior contrasts to what has been reported for Ge–transition-metal interfaces where a reaction barrier precludes intermixing.

INTRODUCTION

Recent photoemission experiments have shown the inequivalence of transition-metal/semiconductor and semiconductor/transition-metal interfaces formed at 300 K. For example, interdiffusion produces extended interfaces when Cr is deposited onto either Ge(111) or a-Ge, but no intermixing was observed for the inverted Ge/Cr or Ge/Ta(110) interfaces.[1-3] In contrast, reactions at Si/Au and Au/Si interfaces have recently been described as symmetric[4] with an extended alloyed transition region between the semiconductor and metal.

As part of an effort which seeks to understand reactions at metal/semiconductor and semiconductor/metal interfaces, we undertook a detailed investigation of the Au-Ge system. Our purpose was to examine the symmetry or asymmetry of interface development by evaluating the formation of any reaction products. We have used synchrotron radiation photoemission to probe both the valence bands and the core levels for interfaces prepared and studied under identical conditions. As will be discussed, core-level spectra provide information about the interface morphology and the distribution of interfacial reaction products. Valence-band spectra reveal the Au $5d$ crystal-field splitting, and this can be correlated with the formation of Au-semiconductor alloys, as shown in prior studies of Au/Ge (Refs. 5 and 6) and Au/Si (Refs. 7–10).

Our results show that there are asymmetries in the distribution of reaction products in these extended interfaces. In particular, although reaction at both interfaces produces the same Au-Ge product, the coverage range over which it forms is very narrow for Ge/Au but is very wide for Au/Ge. When the product ceases to form for Ge/Au, we observe the evolution of an overlayer composed of a-Ge with Au in solution and, ultimately, pure a-Ge. These differences are discussed in terms of diffusion rates of Au and Ge through the reaction product. Finally, our results

agree with those of others that the basic composition is close to the eutectic composition of 28 at. % Ge in Au or approximately Au_3Ge. In this paper, we refer to the composition of this mixture as the Au_3Ge-like or eutectic composition. It should be understood, however, that the use of the phrase eutectic composition does not imply phase separation as would occur when a melt of the eutectic composition is cooled below the eutectic temperature (361 °C for Au-Ge) with decomposition into the terminal solid solutions of Au in Ge and Ge in Au in ratios dictated by the lever rule.

EXPERIMENTAL DETAILS

The photoemission experiments were carried out at the Tantalus I storage ring, at the Synchrotron Radiation Center (Stoughton, WI). Core-level and valence-band studies were conducted in the photon energy range from 40 to 120 eV using monochromatic radiation from the Grasshopper Mark V beam line. The emitted photoelectrons were energy analyzed using a double pass cylindrical mirror analyzer with resolution of 200–250 meV. Core-level shifts were determined with an accuracy of better than 50 meV.

All of the thin-film substrates were prepared by evaporation onto a flash-cleaned Ta foil at pressures better than 2×10^{-10} Torr. Germanium and gold films were deposited from molten droplets confined in tungsten wire baskets mounted about 30 cm from the target. A quartz-crystal thickness monitor was used to measure and control the evaporation rule. For small coverages or for small increments in coverage, we used timed evaporations with typical rates of 0.5–1 Å per minute. In all cases, the samples were held at room temperature. Low-energy electron diffraction (LEED) investigations of the thick gold substrates showed sufficient long-range order to produce a diffuse fcc (111) pattern. The thick as-deposited Ge sub-

High-resolution electron energy loss spectroscopy as a probe of surface morphology and electronic states at metal/semiconductor interfaces

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The covering and consumption of sp^3 hybridized Si atoms in reactions between a metal and Si(111) are monitored by the use of a chemical probe—atomic hydrogen. The surface vibrational spectrum of H on Cu/Si(111) has been measured at various stages of interface growth. The presence of Si atoms with dangling bonds results in covalent bonding with free H atoms, as seen in the Si–H stretching and bending modes in the HREELS spectrum. As Cu is deposited, the morphology of the surface layer can be deduced by observing the disappearance of Si–H vibrational excitations and correlating with Si $2p$ photoelectron line shape and attenuation behavior. The picture which emerges from this analysis is that Cu atoms form clusters from 0 to 3 Å and that at 3 Å the clusters disrupt the surface and trigger outdiffusion of Si. Atomic hydrogen also constitutes a powerful probe of surface electronic states. Previous Auger electron diffraction measurements on the annealed 1 ML Cu/Si(111) interface showed that the surface reconstructs to a planar arrangement with Cu atoms in the hollow sites, and suggested that strong overlap occurs between Cu $4s$ and Si $2p$ orbitals normal to the surface. This result is confirmed by the inertness of the interface to atomic hydrogen.

Evaporation of metal atoms onto semiconductor surfaces at room temperature often leads to bond breaking and chemical reaction above some critical coverage.[1] The morphological structure of the metal overlayer at the onset of reaction is of considerable importance in understanding the driving force behind the reaction. Recently, Zunger[2] proposed that the dissolution of metallic clusters can provide the necessary energy to overcome the activation barrier for intermixing; experimental evidence for this mechanism has been reported for Ce/Si(111), V/Ge(111), and Al/GaAs(110).[3] The key question is whether the metal is clustered or more uniformly spread at the time of reaction. Conventional Auger and photoelectron spectroscopy cannot answer this question because of the persistence of the substrate signal once the surface has been completely covered, often making spectra from surfaces with different morphologies indistinguishable.

In this paper, we describe the use of a chemical probe to detect the presence of surface Si atoms with dangling bonds at various stages of interface development. We have "titrated" a Si(111) surface with atomic hydrogen after first depositing small quantities of Cu, a metal whose interaction with Si has been studied in detail.[4-7] The key experimental measurement is the surface vibrational spectrum using high-resolution electron energy loss spectroscopy (HREELS). The *presence of dangling bonds* enables the formation of covalent bonds with atomic hydrogen,[8] and, as we will show, Cu coverage and subsequent chemical modification of the Si surface by reaction with Cu are directly reflected in the vibrational spectrum.

HREELS measurements were performed on a Leybold-Heraeus ELS22 spectrometer operated by the NSF Center for Research in Surface Science and Submicron Analysis (CRISS) at Montana State University. Parallel synchrotron radiation photoemission measurements were carried out at the Tantalus facility at the University of Wisconsin at Madison and employed the Mark II grazing incidence monochromator. Angle-resolved Auger and He resonance photoemission experiments were performed at the Microelectronic Interface Research Laboratory at the University of Minnesota.

Si(111) wafers were chemically etched and heated to 950 °C under ultrahigh vacuum conditions to produce the 7×7 reconstruction. Si(111)-2×1 surfaces were obtained by cleaving at $\sim 5 \times 10^{-11}$ Torr. Cu deposition was carried out at pressures in the low 10^{-10} Torr range and was monitored with a quartz crystal oscillator. Hydrogen exposure was done by backfilling the chamber to 1×10^{-6} Torr and placing the sample near a hot tungsten filament. All HREELS measurements were performed in specular reflection at an angle of incidence of 60°. The primary beam energy was 6 eV.

Extensive structural and compositional measurements on the Cu/Si(111) interface have been made recently in our laboratory.[6,7] Our results, and those of others,[4,5] have shown that room-temperature deposition of Cu disrupts the surface. Si outdiffuses into the Cu overlayer for coverages greater than ~ 2 Å [1 Å = 1.1 monolayer (ML) on Si(111)]. Details of the atomic distribution in the interfacial region have been extracted from polar-angle-resolved Auger electron emission measurements and related model calculations for varying Cu thicknesses. The best description of the interface is that of Cu metal film of nearly constant density with Si dissolved in the matrix. The average Si density falls off exponentially from the interface boundary and maintains

Summary Abstract: Reaction and epitaxy at the Co/Si(111) interface

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We have combined high-resolution, core level photoemission spectroscopy with high-energy Auger electron diffraction to investigate the chemistry and structure of the Co/Si(111) interface as a function of overlayer coverage and temperature. This system is of special interest because recent transmission electron microscopy (TEM) work has demonstrated that the deposition of thick films of Co (~ 100 Å) at room temperature onto Si(111)-7×7 substrates, followed by annealing at 800–950 °C, results in the formation of an ordered, epitaxial, B-type $CoSi_2$ phase.[1-3] Epitaxy is made possible by the excellent lattice match between Si and $CoSi_2$ (misfit of 1.3%). It is therefore of interest to correlate the chemical and structural properties directly at the $CoSi_2$/Si interface, particularly inasmuch as this interface acts as a template for the growth of the epitaxial heterostructure $Si/CoSi_2/Si$.[4] Since the bulk of this work has been published elsewhere,[5,6] we present only the key results here.

Upon addition of 1 Å of Co, the high-resolution synchrotron radiation photoemission spectrum of the Si $2p$ core level shows the appearance of a chemically shifted feature at 0.3-eV higher binding energy relative to the substrate. This feature grows in intensity as the coverage is increased to 3–4 Å, but diminishes at higher coverages. Since valence-band photoemission spectra in this coverage range are very similar to those for bulk $CoSi_2$,[7-9] we conclude that the initial reaction product is $CoSi_2$ and that it grows in the form of clusters. The latter conclusion is based on the fact that, at its maximum value, the reacted peak intensity reaches only $\sim 15\%$ of the clean-surface Si $2p$ value, suggesting partial coverage of the substrate. At coverages between 4 and ~ 10 Å, we observe the appearance and growth of a second distinct feature at a binding energy of -0.4 eV relative to the substrate. This peak is due to the formation of a solid solution of Si in Co, in basic agreement with electron energy-loss fine-structure measurements of Chainet *et al.*[10] For coverages above 10 Å, the intensity of this second feature falls exponentially, suggesting that the interfacial region is buried with elemental Co. The room-temperature interface is therefore a heterogeneous composite of $CoSi_2$ and dilute solution; it is only about 10 Å thick and is sandwiched between elemental Co and the Si substrate.

The deposition of one monolayer (ML) of Co (1 Å is equivalent to 1.17 ML) onto Si shows a high degree of structural disorder at room temperature. Upon annealing at 500 °C for 2 min, the $CoSi_2$ phase becomes very well ordered. Moreover, the intensities of both the Co MVV and Co LMM Auger lines drop as a result of annealing, indicating the intermixing of Co and Si. We have measured the $L_{2,3}M_{4,5}M_{4,5}$ Auger angular distributions (771 eV) for these annealed interfaces and find that they are in very good

agreement with those calculated by a straightforward kinematical scattering formalism[11] in which a B-type $CoSi_2$ structure is assumed. Detailed comparisons of theory and experiment show that the only structure compatible with the measured angular distributions is one in which epitaxial $CoSi_2$ clusters (or patches) form for coverages of ~ 1 ML equivalent. These clusters are two to three monolayers deep, are oriented so that the [011] direction on the silicide is rotated 180° about the surface normal relative to that of the substrate (B-type $CoSi_2$), and are terminated by a Si(111) bilayer. The orientation of the Si(111) surface bilayer also appears to be antiparallel to that of the Si substrate (i.e., the bilayer stacking sequence appears to be opposite to that of the underlying Si). Polar angle intensity distributions of the interface prepared by depositing the equivalent of one and two monolayers of Co and annealing at 500 °C are virtually identical to those obtained for 30 monolayer equivalents annealed at 700 °C. Inasmuch as the latter is known by TEM measurements to form B-type $CoSi_2$,[1-3] these results support those reached by our comparison between predicted and measured Auger diffraction results. The effect of annealing the ultrathin $CoSi_2$/Si interface then appears to enhance long-range order and bury the $CoSi_2$ clusters beneath the terminal Si bilayer. This increases the near-surface Co coordination number from six to seven, which is closer to the value of eight in bulk $CoSi_2$ and, therefore, is thermodynamically preferred.

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Chemical bonding in ordered Ce overlayers on Si(111)

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Ordered Ce overlayers on Si(111) surfaces having $\sqrt{3} \times \sqrt{3}$ and 2×2 structures with metal coverages of about $\frac{1}{3}$ and $\frac{1}{4}$ monolayers, respectively, have been prepared and studied by synchrotron-radiation photoemission. The valence-band and core-level spectra show that the Ce-Si chemical interaction increases along the series 2×2, $\sqrt{3} \times \sqrt{3}$, and bulk $CeSi_2$, which is associated with increasing Si coordination for the Ce atom. The results are shown to be consistent with cluster-induced reaction and subsequent heterogeneous interface formation at the Ce/Si(111) interface. They suggest the importance of the interplay between Ce—Si, Si—Si, and Ce—Ce bonding in determining interface structures and chemistry.

Metal overlayers deposited on clean semiconductor surfaces often exhibit critical coverage behaviors: Strong chemical reaction or intermixing between the metal and the substrate occurs above a critical coverage (ranging from submonolayer to a few monolayers), while chemical interaction is significantly weaker below this coverage.[1-7] As a driving force for triggering strong interaction, clustering of metal atoms and cluster ripening have recently been proposed for Al/GaAs(110),[8] Ce/Si(111),[9] and V/Ge(111).[10] In these systems, the adatom-substrate bonding at low coverages was postulated to be very weak on the basis of total-energy calculations[8] and thermodynamical arguments.[11] As a result of clustering and cluster ripening, the reacted interfaces are highly disordered, and reaction proceeds heterogeneously rather than uniformly.[12] This complicates detailed studies of the electronic structure and chemical bonding of these interfaces.

In this paper, we report on the formation of ordered structures of Ce overlayers on Si(111) surfaces, and discuss their electronic structures and chemical bonding. Two different structures have been observed, namely a $\sqrt{3} \times \sqrt{3}$ structure for $\Theta \simeq \frac{1}{3}$ monolayer (ML) (1 ML = 2.6 Å = 7.8 × 10^{14} atoms/cm^2) and a 2×2 structure for $\Theta \simeq \frac{1}{4}$ ML. These two ordered overlayers are shown to have significantly different electronic structures: The Ce-Si chemical interaction for the 2×2 overlayer is weaker than for the $\sqrt{3} \times \sqrt{3}$ overlayer. As the ordered structures were produced by heat treatments, the present overlayers are expected to represent more stable structural and chemical states at given metal coverages than as-deposited overlayers prepared at room temperature.

Clean Si(111)-7 × 7 surfaces were prepared by repeated Ar+ sputtering and annealing. Ce was deposited with an evaporation rate of ~1 Å/min at ~1 × 10^{-10} Torr. The amount of deposited Ce was measured with an oscillating quartz crystal. Heat treatments were done by heating or electron bombardment using a filament at the rear of the wafer sample. Changes in the Ce content of the overlayer after heat treatments were monitored from Auger peak heights. The photoemission experiments were performed at the Wisconsin Synchrotron Radiation Center using a toroidal-grating monochromator and a double-pass cylindrical-mirror analyzer. All measurements were done in a pressure of ~5 × 10^{-11} Torr.

Low-energy electron diffraction (LEED) studies of as-deposited surfaces showed a faint 1 × 1 pattern for $\Theta \lesssim 0.3$ ML and no spots for $\Theta \gtrsim 0.3$ ML, consistent with the results of Ref. 9. The samples were then heated in increments of ~50 °C starting from ~250 °C for 5–10 min at each temperature. The heat treatments caused diffusion of Ce atoms into bulk Si,[13] and decreased the number of Ce atoms on the surface. When surfaces with an initial coverage of 0.3–1 ML were heated to ~350 °C, extra spots corresponding to a $\sqrt{3} \times \sqrt{3}$ superstructure were observed, and the Ce coverage in this stage was found to be $\Theta = 0.35 \pm 0.07$ ML. Further heating to ~450 °C (or heating of surfaces with coverages of ~0.2 ML of Ce up to ~350 °C) resulted in a 2×2 LEED pattern and $\Theta = 0.20 \pm 0.03$ ML. From the periodicities of the superstructures and the Ce coverages, the ideal $\sqrt{3} \times \sqrt{3}$ and 2×2 structures should have coverages of $\Theta = \frac{1}{3}$ and $\frac{1}{4}$ ML, respectively. We then conducted synchrotron-radiation photoemission studies of these ordered overlayers to investigate the electronic interactions at the surfaces.

Figure 1 shows typical energy distribution curves (EDC's) for Ce/Si(111)-$\sqrt{3} \times \sqrt{3}$ and -2×2 overlayers in the valence-band region taken at $h\nu = 30$ eV, where one can see a striking difference between the two surfaces. At this photon energy, the Ce $5d$ cross section is much greater than that of the Si sp valence states or the Ce $4f$ level according to calculations on free atoms.[14] In order to further highlight the emission due to the adatoms, we have subtracted the bulk Si emission (with surface states omitted) and obtained the difference curves of Fig. 1. This has been done by varying the weight of the subtracted spectrum, with account taken of the theoretical atomic-orbital cross sections and the photoelectron escape depths. The difference spectrum for Ce/Si(111)-2×2 exhibits two narrow peaks, the stronger one at ~1.5 eV and the weaker one at ~3.5 eV below the Fermi level E_F. The difference spectrum for Ce/Si(111)-$\sqrt{3} \times \sqrt{3}$ also shows a peak at ~1.5 eV, but emission at higher binding energies is stronger and broader than for 2×2 (extending

Core-level binding-energy shifts, thermodynamic predictions, and morphologies for metal-Si and metal-Ge interfaces

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High-resolution core-level photoemission results show two or more distinct reacted chemical species for a wide variety of metal-Si and metal-Ge interfaces. Assuming that the first reacted species at the interface have ~50 at. % Si (or Ge) and the second species are solid solutions of Si (or Ge) in metal matrices, we find reasonable agreement between calculated and experimental chemical shifts. These analyses allow correlation between the reaction products observed at metal-semiconductor interfaces and the bulk thermodynamic properties of the constituents. These results are in agreement with those obtained from a morphological model for evolving interfaces developed by Butera, del Giudice, and Weaver.

INTRODUCTION

In the last decade, a large amount of experimental work has been done to characterize and understand metal-semiconductor interfaces.[1,2] Today, it is recognized that reacted interfaces are the rule rather than the exception. Indeed, high-resolution core-level photoemission has identified distinct chemical shifts in the semiconductor atomic core levels which are indicative of reaction.[3,4] The intriguing chemical and physical processes observed for these metastable systems are ultimately responsible for the complex morphologies of extended interfaces.[5,6] These results have a direct impact on thin-film technologies and microelectronic device fabrication.[7,8]

Several qualitatively different phenomena occur when metal adatoms are deposited onto semiconductor surfaces.[9] In some cases, adatom aggregation and island formation is observed because the interaction between metal atoms is stronger than interaction with the substrate. In others, layer-by-layer growth (possibly epitaxial) is observed.[10-15] Very frequently, however, there is substrate disruption and room-temperature intermixing.[16-18] Interestingly, these reactive systems also exhibit differences at low coverage (0-2 ML) related to adatom clustering as a precursor stage of reaction, on the one hand, and sudden reaction of the impinging metal atom, on the other.[19-21]

Once initiated, reaction is controlled by atomic diffusion as semiconductor atoms out-diffuse through the overlayer, probably via grain boundaries, to reach the reaction sites.[22,23] This appears to be the case for the transition-metal and rare-earth-metal overlayers. As metal deposition continues, the reacted layer thickens and it becomes an increasingly efficient diffusion barrier. Hence, the number of semiconductor atoms available for continued reaction on the metal side of the diffusion barrier decreases and the growing layer converges to a metallic film. In contrast, different overlayer morphologies are observed when the metal atoms are the diffusing species,[24] as for the case for Al,[25] some noble,[26,27] and

the near-noble metals.[28,29] Some of these metals (Cu, Pt, Pd) are characterized by extended interdiffusion with the substrate and a thin solid-solution (or segregated) layer is sometimes formed at the surface (Au, Pd, Cu). Al, which exhibits limited intermixing with the substrate, appears to be the exception.

Insight into the growth characteristics of these systems can be gained through analysis of high-resolution core-level photoemission results. These photoemission spectra are obtained by following the changes in line shape of the Si $2p$ and Ge $3d$ core levels during the evolution of the interface. Subsequent quantitative line-shape decomposition of the core emission makes it possible to chart the growth and decay of each of the reaction products at the interface within the probed region. These intensities (termed attenuation curves) give information about interface morphologies and, less directly, the average stoichiometries of the species which form.[30,31] As we will show here, the chemical shifts are also directly related to the heats of formation (or solution) of the respective species, and these give independent insight into interface constituents and morphology.[32]

In this paper, we discuss the origin of the Si $2p$ and Ge $3d$ chemical shifts for simple-, transition-, noble-, and rare-earth-metal overlayers. We focus on the two reacted species which have been observed during interface formation.[33] From spectroscopic information and modeling of the morphological development of the interface, these have been identified as silicide or germanide phases and solid solutions.[30] Starting from these observations, we use a thermodynamical model to correlate the composition of the reaction product with the measured chemical shifts. Similarities and differences for a variety of interface systems will be examined, and the limitations of the model will be discussed. The major conclusions of this paper are (a) chemical shifts observed at metal-semiconductor interfaces can be explained in terms of compound or solution formation; (b) the first reacted components exhibit chemical shifts which are consistent with the formation of a compound having

Temperature-dependent interface evolution:
Modeling of core-level photoemission results for V/Ge(111)

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High-resolution synchrotron-radiation core-level photoemission results are presented which show the evolution of the V/Ge(111) interface for temperatures between 300 and 643 K. These results have been analyzed quantitatively using an extension of a model developed by Butera, del Giudice, and Weaver to determine the range over which the various reaction products form at each temperature. We find that the reaction product V_2Ge_3 forms over a greater range of coverage with increasing temperature, that the amount of the Ge-in-V solution phase diminishes as thermal transport promotes V_2Ge_3 formation, and that a V-in-Ge solution phase forms, probably in the V_2Ge_3 grain boundaries. The effects of increasing the substrate temperature can be accounted for by a single activation energy which describes these growth profiles and allows the prediction of the interface evolution at any temperature in the range of study.

INTRODUCTION

The physical and chemical properties of metal-semiconductor interfaces have attracted a great deal of experimental and theoretical interest.[1-13] Numerous studies have sought an understanding of the complex reaction chemistry and intermixing observed at interfaces, and great progress has been made. Although we are still far from being able to predict the properties of an interface as a function of temperature and growth conditions, ongoing investigations which focus on the reactivity of the constituents, the composition, spatial extent, and morphology of an interface at each stage in its development, the thermal and environmental stabilities of interfaces, and their electrical behaviors are making substantial headway.

In this paper we present results which shed light on the temperature-dependent evolution of a representative reactive metal-semiconductor interface—V/Ge(111). By using high-resolution synchrotron-radiation core-level photoemission, we have been able to follow the changing chemical environments of Ge atoms at the interface for temperatures $300 \leq T \leq 643$ K. We have used these results to examine the limitation of a recently developed model for the room-temperature evolution of that interface.[12] The goal of that model, and its extension here, was the elucidation of factors which govern the formation of reactive metal-semiconductor interfaces. Here, we show that it is possible to determine the temperature-dependent parameters which control the evolving interface.

The earlier study[12,13] showed that the V/Ge(111) interface is composed of the Ge substrate, a heterogeneous polycrystalline V_2Ge_3 phase which forms on the Ge substrate, a solid solution of Ge in V over the V_2Ge_3 phase,

and an overlayer of pure V which terminates at the vacuum surface. We will show here that the V_2Ge_3 and the solution phases persist as the temperature is increased but that the spatial extent of each phase changes. The enhanced growth of the V_2Ge_3 phase follows an exponential of $-1/T$. Likewise, we show that there is a new phase which is formed as the temperature is increased, namely, a dilute V-in-Ge phase which probably grows in the V_2Ge_3 grain boundaries. The amount of this phase also increases exponentially as $-1/T$, with the same energy parameter as for the thickening of the V_2Ge_3 phase. These results show a metastable interface, but the modeling presented herein makes it possible to describe the evolution quantitatively over a wide range of temperatures.

EXPERIMENTAL TECHNIQUES AND RESULTS

High-resolution core-level photoemission studies were conducted at the Wisconsin Synchrotron Radiation Center using the grasshopper Mark-II monochromator and beam line. The overall instrumental resolution was 250 meV (electrons plus photons). An etched Ge(111) wafer was cleaned by Ar-ion sputtering and thermal annealing cycles at 875 K. The cleanliness and quality of the surface was determined with Auger spectroscopy and valence-band photoemission. The temperature of the sample was controlled by a resistive heater attached to the holder. The temperature was stabilized before the first evaporation cycle was begun, and the overall thermal stability was ±5 K throughout each series of measurements. The results reported for each isotherm were found to be independent of time, indicating steady-state conditions. For each experiment, vanadium was evaporated onto the cleaned Ge(111) surface from a

Abruptness of Au-Si contacts with thin CoSi₂ interlayers

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High-resolution synchrotron radiation photoelectron spectroscopy has been used to study Au/Si and Au/CoSi₂/Si interface formation at room temperature. Our results show Au-Si intermixing, the absence of a well defined Au-Si compound, and surface segregation of small amounts of Si to the Au surface. An interlayer formed by the deposition of < 3 Å of Co has relatively small effect on this Au-Si atomic profile. Intermixing is abruptly quenched, however, when the Co deposition exceeds 3.5 Å, and a Au film free of Si can grow on the CoSi₂ layer. These results demonstrate the effectiveness of CoSi₂ layer as a barrier against Au-Si intermixing and identify the critical coverage of Co needed to passivate the Si surface.

The Au/Si interface has attracted a great deal of attention because of the use of Au metallizations in integrated circuit technologies. Early work envisioned Au as a prototype metal overlayer, but recent studies have shown that Au contacts are remarkably complex. There is consensus that Au deposition onto Si induces disruption of the Si surface, although the extent of the intermixing has not been clear. Studies which emphasize the surface region of a Au/Si junction show a region rich in Si, and this is variously termed an alloy or a Au,Si-like compound.[1-7]

In this letter, we show that Si substrate disruption and Au-Si intermixing can be controlled by the deposition of small amounts of Co onto Si. Co was chosen as the interlayer material because the epitaxial growth of CoSi₂ on Si has been well documented, even at room temperature,[8-11] and because CoSi₂ may offer the opportunity of forming a nearly perfect diffusion barrier free of grain boundaries. By examining the details of Au/Si interface formation with interlayers of Co grown by depositing 0.5 to 12 Å, we have determined the coverage at which the Si surface is passivated against Au-induced disruption. This passivation makes it possible to form a Si-free Au overlayer on the stable CoSi₂ interlayer. These results offer insight into the physical mechanisms of interdiffusion and mass transport, and they indicate that an abrupt, stable, metal-semiconductor junction can be formed. Our results correlate intermixing to changes in chemistry, growth morphology, and structure of the CoSi₂/Si interface.

In order to characterize reaction and intermixing at Au/CoSi₂/Si interfaces, we examined the Si 2p core level emission as a function of Au and Co coverage using surface sensitive and bulk sensitive photoemission. Detailed line shape analyses and intensity measurements made it possible to assess the atomic distribution and chemical states of Si at the interface. The experiments were conducted at the Aladdin electron storage ring at the University of Wisconsin using the Mark II Grasshopper monochromator and beamline. The photon energies were 109 and 135 eV to give Si 2p photoelectron mean free paths, λ, of 20–24 Å and 3–5 Å, respectively, and probe depths of 3λ.[12] High-quality Si(111) 2×1 surfaces were obtained by cleaving p-type single-crystal Si bars *in situ* at pressures of 5 · 10⁻¹¹ Torr. A double pass cylindrical mirror analyzer was used for photoelectron energy analysis. The overall energy resolution (photons

+ electrons) was 0.2–0.4 eV. Co and Au were evaporated from W boats at pressures better than 2 × 10⁻¹⁰ Torr, and the depositions were monitored with a quartz oscillator. The overlayer thicknesses were determined by timed exposures to the sources after the evaporation rate was fully stabilized (rate ~ 1 Å/min, sample to source distance ~ 30 cm).

In Fig. 1 we show the evolution of the Si 2p core emission taken at a photon energy of $hv = 135$ eV at representative Au coverages with Co interlayer thicknesses of zero (left panel), 3 Å (middle panel), and 4.5 Å (right panel). All energy distribution curves (EDC's) have been background subtracted and normalized to highlight line shape changes. Band bending effects have been removed to facilitate assessments of chemical changes. The bottommost curve on the left is for the cleaved Si(111) 2×1 surface and shows the bulk and surface-shifted $2p_{1/2,3/2}$ components.[12] The surface components are rapidly lost when metal adatoms are deposited.

Room-temperature Au-induced disruption of the Si substrate can be easily seen through the appearance of a shoulder on the high binding energy side in the Si 2p EDC, even for $\theta = 1$ Å (left panel of Fig. 1). In the low coverage range (< 5 Å), this feature grows in relative intensity, shifts from the substrate peak to greater binding energy, and broadens. This suggests that a heterogeneous, intermixed region forms with a variety of Au-Si bonding configurations. With increasing Au coverage, however, the Si 2p EDC's sharpen while continuing to shift, slowly, to higher binding energy (total shift by 120 Å Au deposition is 0.7 eV). This indicates that the distribution of Si in the near surface region becomes more uniform and that Si atoms are dissolved in the Au matrix or are dispersed on the surface.

Additional insight into the distribution of Si in the overlayer can be gained by plotting the Si 2p core intensity as a function of coverage, θ, defined as $\ln[I(\theta)/I(0)]$, where $I(0)$ is the intensity for the clean surface. In the upper panel of Fig. 2 we show these attenuation curves for two photon energies where the energies were chosen to vary the probe depths, 3λ, from ~ 10 Å for 135 eV to ~ 60 Å for 109 eV. The attenuation is rapid at low coverage but is much more gradual after ~ 10 Å. Indeed, the greater the surface sensitivity the greater the relative emission at high coverage. These results provide clear evidence that the overlayer is *not*

High-resolution photoemission study of Co/Si(111) interface formation

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We have examined the formation of the Co/Si(111) interface at room temperature using high-resolution core-level photoemission spectroscopy. Two chemically shifted Si $2p$ core-level components have been identified. The evolution of these components with Co coverage makes it possible to model the development of this interface. Heterogeneous $CoSi_2$-like cluster formation is observed for nominal Co coverages of less than ≈ 4 Å. Continued reaction to form $CoSi_2$ becomes diffusion limited when the clusters coalesce, and a solid solution forms with Si atoms in a Co matrix. For Co coverages of more than 8–10 Å, the interfacial region is buried by a metallic Co film.

INTRODUCTION

Investigations of the nature of metal-semiconductor interfaces are important for both technological and scientific reasons.[1] Recent studies of interface morphologies have shown that metal-semiconductor junctions are generally not abrupt on the atomic scale and that atomic intermixing can produce a variety of different boundary-layer profiles.[2] These include thin silicide layers which form for Ce/Si(111) following cluster-induced reaction,[3] nearly perfect silicide-silicon interfaces for NiSi₂/Si,[4] and asymmetries of formation for metals on semiconductors compared to semiconductors on metals.[5] Important objectives in such studies include the characterization of the properties and physical extent of the (metastable) reaction products which form when metal atoms are deposited onto semiconductor surfaces under controlled conditions.

For the Co-Si and Ni-Si systems, it has been shown that annealed interfaces exhibit epitaxial disilicide growth.[4] For Co/Si(111) the disilicide structure is rotated 180° about the surface normal, forming the so-called B-type silicide, while both the rotated and unrotated types exist for Ni/Si(111). There has been a great deal of excellent characterization of these lattice-matched interfaces, including correlations between the structure type and the Schottky barrier.[6] Further, transistor-like devices have been fabricated based on Si/CoSi₂/Si layers.[7] In our own laboratory, we have used angle-resolved Auger electron spectroscopy to examine the structure of very thin CoSi₂ layers formed by Co deposition onto Si(111) and annealed according to the recipe of Tung.[6] Those results indicated that B-type CoSi₂ clusters form at very low coverage and are terminated by a Si(111) bilayer.[8] These clusters are 2–3 unit cells in thickness. For nominal Co depositions of 1 monolayer (ML), we found a heterogeneous surface of Si(111) decorated with B-type CoSi₂.

The present study was undertaken to examine the boundary layer that forms at room temperature, with particular interest in the growth of the silicide when the reaction itself is impaired by kinetics and diffusion limitations. Although less is known about room-temperature growth than about the formation of the interface at higher tem-

perature, two interesting studies have been reported. Pirri et al.[9] used angle resolved photoemission to study the valence bands, low-energy electron diffraction (LEED) to investigate ordering, and x-ray photoemission to follow changes in the core-level signatures. Chainet et al.[10] used surface electron-energy-loss fine-structure spectroscopy (SEELFS) to determine Co—Si bond lengths at the evolving interface. These authors noted the similarities of Co/Si with the more extensively studied Ni/Si system.[11]

In this paper, we present high-resolution core-level photoemission results for the room temperature formation of the Co/Si(111) interface. Observed binding energy shifts for the Si $2p$ core levels are used to reveal changes in chemical environment at the interface, and line shape analysis provides insight into the nature and extent of these environments.[12] We have found that a very thin layer of CoSi₂ forms during the early stages of deposition at room temperature. When the formation of the silicide is limited by kinetics, a solide solution phase of Si in Co forms over the silicide layer. The solution phase ultimately yields to an overlayer of pure Co for thick films grown at room temperature.

EXPERIMENT

Photoemission experiments were performed at the Wisconsin Tantalus storage ring using synchrotron radiation that was monochromatized by the Grasshopper Mark V monochromator. Photoelectrons were energy analyzed using a double-pass cylindrical mirror analyzer in an ultra-high vacuum system having an operating pressure of $\sim 5 \times 10^{-11}$ Torr. High purity Ames Laboratory cobalt was evaporated by resistive heating of a degassed 5-mil tungsten boat. The source to sample distance was ~ 30 cm and the evaporation rate, as measured with a quartz crystal oscillator, was approximately 1 Å/min. Evaporations were done at pressures of less than 3×10^{-10} Torr. Submonolayer depositions were done by timed exposures of the sample to the evaporation source. The Si crystals were n type and were oriented for cleavage along the (111) plane. The quality of the cleaved surface was judged visually and with valence band and $2p$ core level spectra.

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Synchrotron Radiation Photoemission
Studies of Interfaces*

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I. Statement of Purpose

The purpose of this chapter is to describe the scientific and technological
advances that can be made by using synchrotron radiation photoemission
in studies of interfaces. We shall show that synchrotron radiation photo-
emission is one of the most flexible probes of surface/interface properties
and, although it is by no means the only probe, it is the technique of choice
for many kinds of research. Much of the discussion will revolve around case
studies and examples of metal-semiconductor and metal-metal interfaces

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CoSi₂ Diffusion Barrier Modulation of Au/Si(111) Interface Reactions

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We report a synchrotron radiation photoemission study of the modulation of intermixing at the Au/Si interface which results from thin $CoSi_2$ interlayers. This study was stimulated by the need to understand atomic intermixing across Si-based interfaces.[1-3] Cobalt was chosen because the epitaxial growth of $CoSi_2$ on Si has been well documented, even at room temperature,[4-7] and this offered the opportunity of forming a nearly perfect diffusion barrier free of grain boundaries. Such a layer could quency Au-induced disruption of Si and allow the formation of a Si-free Au overlayer on the stable $CoSi_2$ layer.

To quantitatively assess reaction and intermixing at $Au/CoSi_2/Si$ interfaces, we examined the Si 2p core level emission as a function of Au coverage for a range of Co thicknesses.[8] We found that a reaction-induced feature grows in relative intensity for the binary Au/Si system, first broadening but ultimately sharpening again as it shifts continuously to greater binding energy relative to the position of Si for the clean surface. As shown at the top of Fig. 1, the integrated Si 2p intensity attenuates very rapidly at low coverage but then diminishes slowly at high coverages (photoelectron mean free path 3-5 Å at hν = 135 eV and 20-24 Å at 109 eV, giving probe depths of ~12 Å and ~60 Å, resp.). This indicates Si enrichment of the surface and near-surface region,[8,9] as indicated schematically in the left panel of Fig. 2. The Si distribution profile can be altered by the deposition of a small amount of Co prior to the growth of the Au film, i.e. by the spontaneous formation of thin layers of $CoSi_2$.[4-7] Of course, the effectiveness of the interlayer as a diffusion barrier depends on its morphology at Co/Si interface.

Our results indicate that the evolution of Si 2p core level lineshape with Au coverage shows

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*The transition region between two solids exhibits properties which are unique
and are difficult to characterize but which are critical for a wide range
of multicomponent materials systems.*

John H. Weaver is Professor of Chemical Engineering and Materials Science at the
University of Minnesota. His research interests in interdisciplinary studies of solid
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SURFACE SEGREGATION

AT EVOLVING METAL / SEMICONDUCTOR INTERFACES[#]

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ABSTRACT

This chapter focuses on the interesting observation that semiconductor atoms segregate to the free surface for many evolving metal/semiconductor interfaces. Their presence contributes to the range of intriguing properties of interfaces and their study offers insight into complicated interface behavior. We review the experimental techniques used to investigate atom distributions across metal/semiconductor interfaces and summarize the results for a wide range of metal overlayers grown under ultrahigh vacuum conditions on Si, Ge, GaAs, InP, and InSb. Simple considerations based on cohesive energies and atomic energies give remarkably good agreement concerning surface segregation.

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